

Design and Synthesis of New Acceptor Molecules for Photo-Induced Electron Transfer Reverse Saturable Absorption

M. BADER*, T. Carvalho, H. LI**, S. TARTER***, C. SPANGLER***

*Department of Chemistry, Pennsylvania State University-Hazleton, Hazleton, PA 18201

**Scientific Materials Corp., 310 Icepond Rd., P.O. Box 786, Bozeman, MT 59715

***Department of Chemistry and Biochemistry, Optical Technology Center, Montana State University, Bozeman, MT 59717, mmbl11@psu.edu

ABSTRACT

With the advent of efficient and relatively inexpensive pulsed and CW laser systems for both civilian and military applications, the need for adequate eye and sensor protection is becoming increasingly important. While it is possible to filter out harmful wavelengths if the laser frequency is known, the proliferation of frequency agile laser sources underscores the need for "smart" passive materials that can sense the incident wavelength and provide protection. There has been considerable progress made in recent years in the design of optical power limiting (OPL) materials that can function by a variety of mechanisms, most of which derive their limiting behavior from some type of nonlinear absorption process. The most well-studied of these processes involve excited state absorption in which the absorption cross-sections of the photo-generated transient species are much greater than the original S_0 to S_1 transition. In this presentation we will discuss the efficacy of charge transfer species for optical limiting, and the need for more and better electron acceptor species.

INTRODUCTION

Most organic molecules and polymers that have exhibited optical limiting behavior in the past have relied on the most prevalent transition being formed during optical pumping of the ground state singlet (S_0) to be triplets (T_1), formed by intersystem crossing (ISC) from the S_1 excited state. If the excited state absorption cross-sections are larger than the S_0 to S_1 cross-section at the excitation wavelength, then the material is usually referred to as a reverse saturable absorber (RSA) and becomes more absorbing as the laser intensity increases. A large number of different structural types display RSA behavior through triplet state absorption, such as indanthrones, metal cluster compounds, porphyrins, phthalocyanines and fullerenes¹. The RSA behavior can be observed when the compounds are studied in solution, or when the chromophores are covalently attached to a polymer backbone or incorporated as guest-host composites. During the past few years, however, we have initiated a project in which we have proposed that transient charge states, either polaronic or bipolaronic, might also be useful as highly absorbing RSA transient states instead of the more familiar triplet states. In this presentation we will review the features of this alternative RSA-OPL mechanism, and why new electron-acceptors might be necessary.

THE DESIGN OF RSA CHROMOPHORES FOR PHOTO-INDUCED ABSORPTION

As stated above, the majority of the examples of RSA behavior in the literature have focused on triplet state absorption. The C. Spangler research group has been examining the formation and stabilization of polaron-like radical cations and bipolaron-like dications by oxidative doping of diphenyl- and dithienylpolyenes and PPV oligomers for several years²⁻⁵. In almost all cases these charge states are much more highly absorbing than the neutral π - π^* transition, and we have postulated⁶ that they may be effective OPLs if they could be photo-generated on a fast time scale (ca 1 ps). Over the same time span, other research groups have addressed the problem of the efficiency of photo-generated charge state formation in conjugated molecules and polymers. Of particular interest to the problem of optical limiting is a recent review by Saraciftci and Heeger⁷ on the photophysics of charge separation between conjugated polymers and fullerenes. C_{60} is a recognized optical limiter based on RSA from the excited state manifold⁸⁻¹⁰. Saraciftci and coworkers have also demonstrated that a photo-induced electron transfer can occur between a conducting polymer, such as MEHPPV or poly[3-alkylthiophene], and C_{60} , which produces different absorption species than either component irradiated individually^{11,12}. Light-induced ESR studies indicate formation of both positive (from donor) and negative (from acceptor) polarons, with concomitant quenching of the photoluminescence. While the above studies were carried out by optically pumping the donor, ideally optical

pumping of the acceptor could lead to the same excited state manifold. Thus RSA behavior in a D/A pair should be observed by either photo-induced electron transfer or photo-induced hole transfer⁷. Janssen and coworkers¹³ have been able to demonstrate photo-induced absorption (PIA) in a series of oligothiophenes in solution, wherein both triplets and radical-cations could be identified. Addition of TCNE quenched the triplet state formation and efficiently produced radical-cations. Other conjugated polymers formed long-lived charge-separated states in the presence of a series of TCNQ derivatives, and finally, composite films of C_{60} and the oligothiophenes display PIA spectra characteristic of polymer radical-cations and fullerene radical anions¹⁴. Examples of donor polymers and electron-acceptors that display this PIA behavior is illustrated in Figure 1.

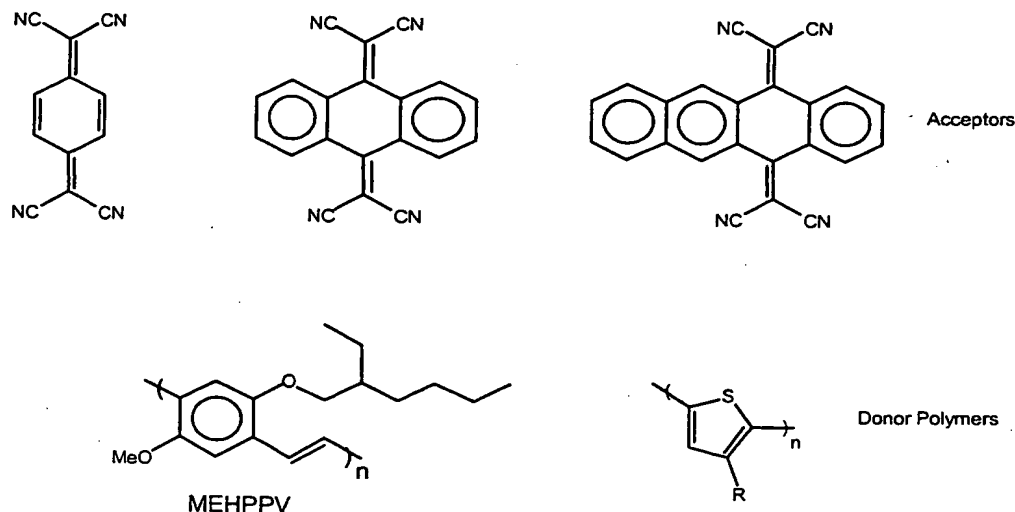
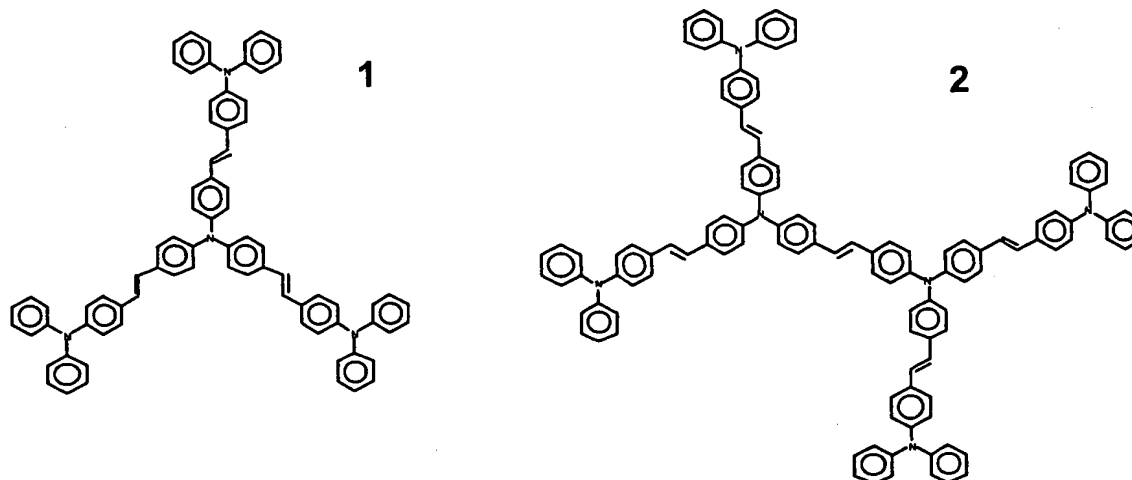


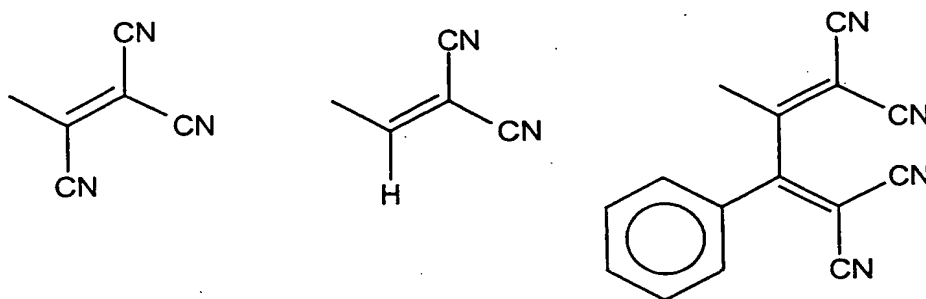
Figure 1. Typical acceptors and donor conjugated polymers that display PIA.

We have recently been examining dendrimers based on bis-(diphenylamino)stilbene repeat units as efficient donor species for PIA RSA. The synthesis of the two G-0 dendrimers, 1 and 2, have been reported recently, and these materials are of interest for OPL due to their stable, highly absorbing bipolaronic charge states¹⁵. The structures of 1 (a three-arm dendrimer) and 2 (a four arm dendrimer) are shown below. We have irradiated these dendrimers in solution in the presence of C_{60} , and observed efficient PIA, and the nature of the charge-states formed (polaronic or bipolaronic) is currently under investigation¹⁶. For the design of practical optical limiting devices, however, it will be necessary to fabricate donor/acceptor pairs as polymer films. We recently have been able to demonstrate that dendrimer 1 can be vacuum deposited as a thin film. The dendrimers can also be spin-coated from solution. While C_{60} is a well-studied and useful acceptor for OPL studies, its relative lack of solubility in common organic solvents makes it difficult to use in practice. Also, if we wish to use acceptor pumping to initiate the PIA, we need to be able to vary the absorption characteristics of the acceptor species. Thus it would be highly desirable to have a number of soluble, efficient electron-acceptors whose absorption characteristics span a wide portion of the Visible spectrum.



DESIGN AND SYNTHESIS OF NEW ELECTRON-ACCEPTORS FOR PIA

Since most of the acceptors that have been shown to initiate PIA with conjugated donor moieties have cyano substituents, we determined to focus on acceptor series having dicyanovinyl, tricyanovinyl and tetracyanobutadienyl functionalities:



We have previously described the preparation of dithienylpolyenes³. These materials are soluble and can be derivatized to yield the bis-(dicyanovinyl) and bis(tricyanovinyl) substituted polyenes in good yield. These preparations are outlined in Figure 2. The phenyltetracyanobutadienyl group is a relatively new acceptor proposed by Jen¹⁷ as an extremely efficient acceptor for second order nonlinear optics applications in donor-acceptor (push-pull) polyenes. This acceptor group has not been examined for other photonics applications, or as an acceptor for photo-induced electron transfer processes.

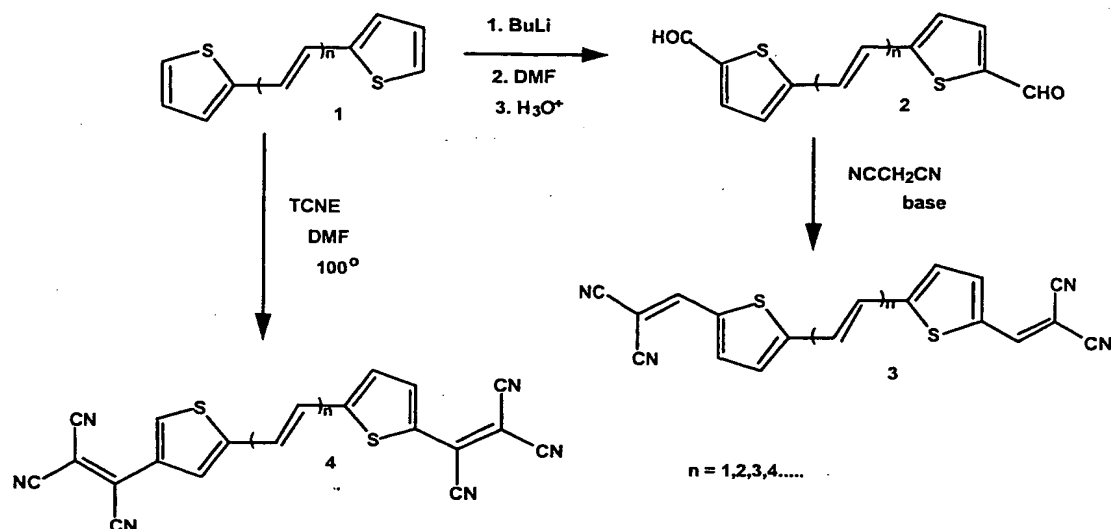


Figure 2. Preparation of bis-(dicyanovinyl) and bis-(tricyanovinyl) dithienylpolyenes.

The derivatized materials are much less soluble than the precursor polyenes, and if the future PIA studies dictate, we might have to add *n*-butyl solubilizing substituents in the 3,4-positions of each thiophene ring. We have also previously described the use of triphenyl amine in the synthesis of bis-(diphenylamino)diphenylpolyenes. The ring positions of the diphenylamino groups can be readily derivatized with $-\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{OAc}$ groups for attachment to polymer backbones (e.g. PMMA) or to 3,5-dihydroxybenzyl alcohol for dendron attachment and subsequent dendrimer synthesis. Thus we have also synthesized triphenylamine moieties with both tricyanovinyl and phenyltetracyanobutadienyl groups, as outlined in Figure 3.

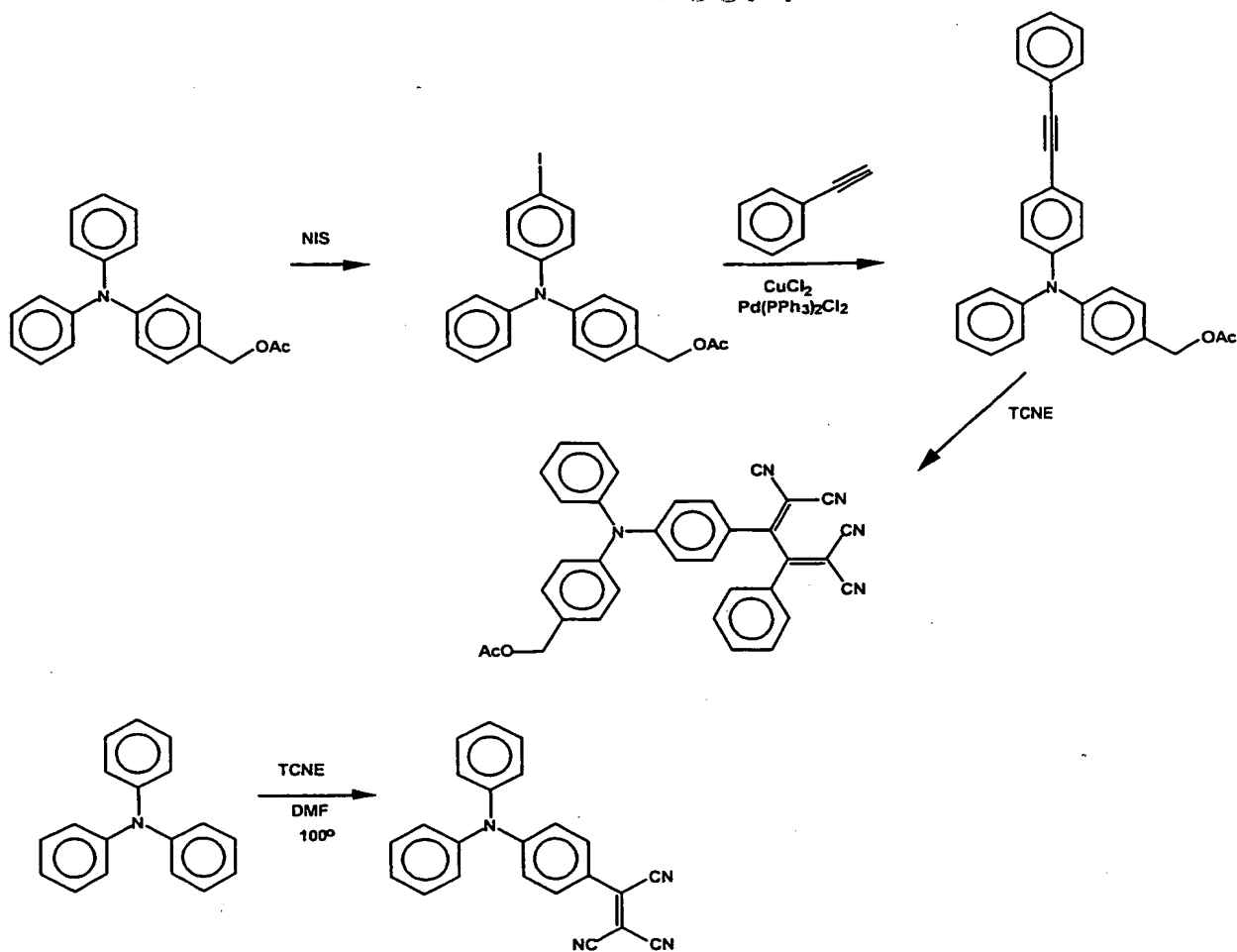


Figure 3. Preparation of tricyano and phenyltetracyanobutadienyl substituted acceptors.

CYCLIC VOLTAMMETRY OF NEW ACCEPTOR CHROMOPHORES

Cyclic voltammetry has become an important tool for the study of the mechanisms of redox processes, particularly in organic and metal-organic systems. There are several pieces of information that can be inferred from cyclic voltammetry. Since the oxidation process corresponds to the removal of electrons from the HOMO band and the reduction process corresponds to the addition of electrons to the LUMO band, one can estimate the band gap or E_g for the material. Based on the values of the cathodic and the anodic peak currents, one can also evaluate the reversibility of such redox processes. Several acceptor molecules were evaluated for their electron-accepting ability by cyclic voltammetry. Table 1 below shows a summary of the CV data for some of these compounds. All compounds showed a reversible or quasi reversible redox behavior, based on the ratio of the anodic to the cathodic current peaks.

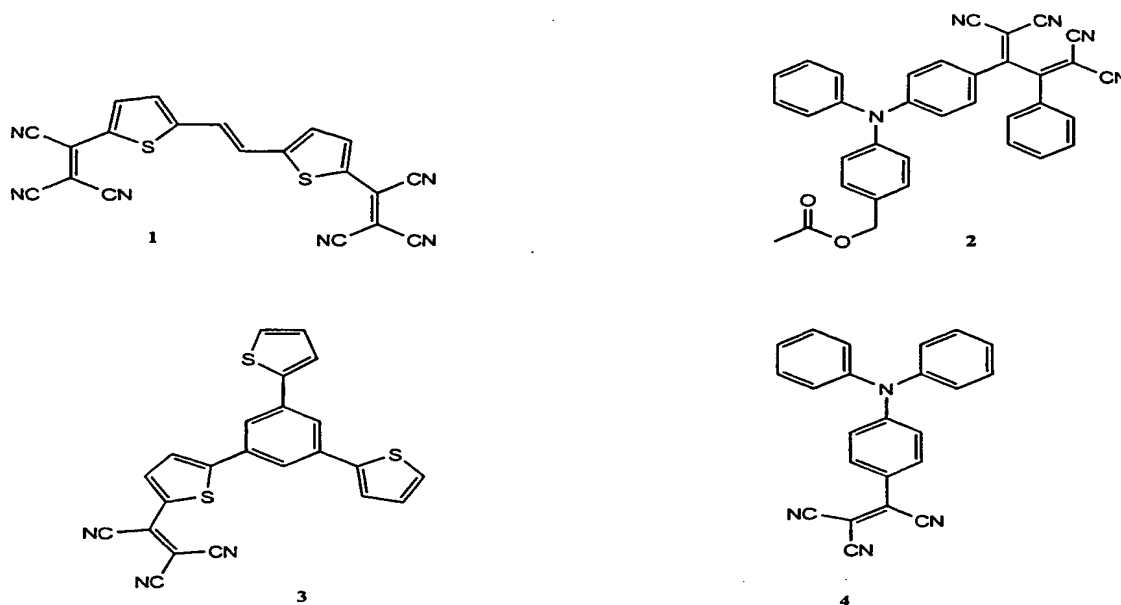


Figure 4. Chemical structures for the samples in Table 1.

Table 1. Electrochemical Characteristics of Some of the New Acceptors Considered in This Study

Sample	$E_1^{1/2}$	$E_2^{1/2}$	ΔE
1	-0.605	-1.488	0.883
2	-0.766	-1.392	0.626
3	-0.586	-1.432	0.843
4	-0.758	-1.312	0.554
TCNQ	-0.120	-0.390	0.510

Data is in V vs. SCE in anhydrous acetonitrile at room temperature, lithium perchlorate was used as an electrolyte, scan rate 100 mV/s.

CONCLUSIONS

In conclusion, we described here our preliminary findings on the synthesis and characterization of a set of new acceptor molecules. Based on these results, we will continue with the preparation of structurally related molecules. Preparation of polymers incorporating these molecules will be pursued.

ACKNOWLEDGMENTS

This research was supported in part by Technical Management Concepts, Inc. under subcontract No. TMC-97-5405-0013-02. Partial support is also acknowledged from the Donors of the Petroleum Research Fund of the American Chemical Society, and MB would like to acknowledge support for this project as an American Chemical Society/Petroleum Research Foundation Faculty Fellow during the Summer, 1999.

REFERENCES

1. C. W. Spangler, J. Mater. Chem. 9, p. 2013 (1999).
2. C. W. Spangler, R. K. McCoy, A. A. Dembek, L. Sapochak and B. D. Gates, J. Chem. Soc. Perkin Trans. 1, p. 151 (1989).
3. C. W. Spangler, P.-K. Liu, A. A. Dembek and K. O. Havelka, J. Chem. Soc. Perkin Trans. 1, p.799 (1991).
4. C. W. Spangler and M. Q. He, J. Chem. Soc. Perkin Trans. 1, p. 715 (1995).
5. C. W. Spangler and M. Q. He, in *Handbook of Conductive Molecules and Polymers: Vol.2. Conductive Polymers: Synthesis and Electrical Properties*, edited by H. S. Nalwa, John Wiley and Sons, Ltd., Chichester, 1997, pp. 389-414.
6. C. W. Spangler and M. Q. He, Mat. Res. Soc. Symp. Proc. 479, p. 59 (1997).
7. N. S. Saraciftci and A. J. Heeger, in *Handbook of Organic Conductive Molecules and Polymers: Vol. 1. Charge-Transfer Salts, Fullerenes and Photoconductors*, edited by H. S. Nalwa, John Wiley and Sons, Ltd., Chichester, 1997, pp. 414-455.
8. L. W. Tott and A. Kost, Nature 356, p. 225 (1992).
9. F. Henari, J. Callaghan, H. Stiel, W. Blau and D. J. Cardun, Chem. Phys. Lett. 199, p. 144 (1992).
10. D. J. McLean, R. L. Sutherland, M. C. Brant, D. M. Brandelik, P. A. Fleitz and T. Pottenger, Opt. Lett. 18, p. 858 (1993).
11. N. S. Saraciftci, L. Smilowitz, A. J. Heeger and F. Wudl, Science 258, p. 1474 (1992).
12. R. A. J. Janssen, D. Moses and N. S. Saraciftci, J. Chem. Phys. 101, p. 9519 (1994).
13. R. A. J. Janssen, M. P. T. Christiaans, C. Hare, N. Martin, N. S. Saraciftci, A. J. Heeger and F. Wudl, J. Chem. Phys. 103, p. 8840 (1995).
14. R. A. J. Janssen, M. P. T. Christiaans, K. Pakbaz, D. Moses, J. C. Hummelen and N. S. Saraciftci, J. Chem. Phys. 102, p. 2628 (1995).
15. E. H. Elandaloussi and C. W. Spangler, Polym. Preprints 39(2), p. 1055 (1998).
16. W. Sonnenberg, A. Hyfield, K. Short, L. Spangler and C. Spangler, Mat. Res. Soc. Symp. Proc. (submitted).